

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY, HARVARD UNIVERSITY]

THE HOMOGENEOUS THERMAL POLYMERIZATION OF 1,3-BUTADIENE

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Association reactions of the type $A + B \longrightarrow C$ have received a very considerable amount of study and have been treated extensively both experimentally and theoretically.² Born and Franck³ have concluded that in the case of atoms such a process as the direct addition would be extremely unlikely, due to the energy present in the two reacting particles, which must be dissipated for stabilization of the product; this could occur on a triple collision or at the walls. Polanyi and Wigner⁴ have discussed the mechanism as a reversal of the optical Auger process or the mechanism of unimolecular decomposition; this leads to results in a formal way similar to those of Born and Franck. The work on the recombination of bromine atoms⁵ and of hydrogen atoms⁶ gives experimental confirmation of the theory in that the rate is within agreement with that calculated from the frequency of triple collisions.

A generalization of this criterion of association reactions to the combination of more complicated molecules has been proposed and it has been thought by some that bimolecular associations as such could not occur. This idea certainly is subject to scrutiny, since there is an urgent *a priori* reason to admit the necessity of the reverse of unimolecular reactions.

The kinetics of homogeneous thermal polymerization reactions have received relatively little attention. Indeed practically the only data available are those of Pease on acetylene,⁷ and on ethylene.⁸ The former of these studies was carried on in a dynamic system and it was shown that between 400 and 600° the process was homogeneous and bimolecular, and somewhat suppressed by the presence of glass packing, indicating a chain mechanism. The latter demonstrated that butylene was the primary prod-

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² See Kistiakowsky, *Chem. Rev.*, **10**, 91 (1932), for a summary of the work on atomic association reactions.

³ Born and Franck, *Z. Physik*, **31**, 411 (1925); also Polanyi, *ibid.*, **1**, 337 (1921); Herzfeld, *ibid.*, **8**, 132 (1922).

⁴ Polanyi and Wigner, *ibid.*, **33**, 429 (1925).

⁵ Jung and Jort, *Z. physik. Chem.*, **3B**, 83 (1929); Jung, *ibid.*, **3B**, 97 (1929).

⁶ Smallwood, *THIS JOURNAL*, **51**, 1985 (1929); Senftleben and Riechemeyer, *Ann. Physik*, **6**, 105 (1930); Steiner and Wicke, *Z. physik. Chem.*, *Bodenstein Festbd.*, **817** (1931).

⁷ Pease, *THIS JOURNAL*, **51**, 3470 (1929).

⁸ Pease, (a) *ibid.*, **52**, 1158 (1930); (b) **53**, 613 (1931).

uct and that again the reaction was roughly bimolecular; further experiments at pressures as high as 10 atmospheres over a temperature range of 350 to 500° in a static system confirmed the bimolecular rate and gave as the energy of activation of the reaction 35,000 cal. At 425° the reaction rate constant as calculated from the formula $Z e^{-E/RT}$ is some 2000 times the experimental value. This was interpreted as showing that only one collision of suitably activated molecules in 2000 has satisfied the energy and quantum conditions. A mechanism was proposed: a quasimolecule is produced by combination of two ethylene molecules; this may be destroyed or stabilized by another collision, provided it does not dissociate spontaneously; it is suggested that the destruction process is 2000 times as probable as the stabilization, and these steps lead to a mechanism which is of second order at high pressure and third order at low. Kassel⁹ has treated this subject theoretically and concludes that in as far as conservation requirements and quantum restrictions are involved, the formation of complex molecules by a bimolecular association process should be possible at a relatively large fraction of all collisions, a conviction not shared by others.¹⁰ Kassel also submits a modification of the earlier mechanism, in which he qualitatively apportions the efficiency factor between the two processes of the formation of the unstable complex upon collision and of the stabilization by impact with another molecule of ethylene. Pease¹¹ has also studied the hydrogenation of ethylene at 475 to 550° and one atmosphere pressure and finds it to be homogeneous and second order; calculations show that 10% of the collisions between hydrogen and the hydrocarbon molecules possessing sufficient energy (43,150 cal.) result in the formation of ethane.

The present set of experiments was initiated at the University of Chicago in 1930 with the intent of lessening the dearth of data in this field. In preliminary work the compound studied revealed itself very capable of thermal polymerization and as such suggested an interesting possibility. As another issue the light absorption of the vapor at one atmosphere pressure in a 20-mm. tube was determined with a Hilger E2 spectrograph; an abrupt long wave length continuous end-absorption limit at 2500 Å. was found. The effect of the total radiations of a discharge in hydrogen and of a very intense high potential spark between cadmium disks¹² was the production of decomposition of the vapor; an analysis of the data proved complex. The study of the thermal polymerization proved, however, to be extremely interesting.

⁹ Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., Inc., N. Y., 1932, pp. 44-47; *THIS JOURNAL*, **53**, 2143 (1931).

¹⁰ See, for example, Taylor and Emel us, *ibid.*, **53**, 562 (1931).

¹¹ Paper presented at the New Orleans meeting, American Chemical Society, April, 1932; *THIS JOURNAL*, **54**, 1876 (1932); also Ref. 8a.

¹² Wiig and Kistiakowsky, *ibid.*, **54**, 1806 (1932).

Experimental

1,3-Butadiene was prepared from the corresponding tetrabromide¹³ which had been made according to the method of Muskat and Northrup.¹⁴ The solid tetrabromide without further purification was brought by extraction with hot alcohol into the boiling flask in which was suspended by vigorous stirring an excess of finely powdered zinc; the butadiene produced by reduction distilled out through a water-cooled spiral condenser and a trap immersed in ice into a pair of traps in series chilled in a carbon dioxide-acetone mixture wherein practically complete condensation occurred. Yields were of the order of 90 to 95%. The liquid product was quite colorless. It was introduced into an evacuated storage system by slow distillation through drying tubes of phosphorus pentoxide or, as was found better, due to some adsorption of the butadiene by the phosphorus pentoxide with subsequent discoloration of the solid, through pellets of sodium hydroxide. The last third of the butadiene was discarded. The drying seemed not to influence the reaction rate as materials produced in either of these ways gave identical results. The gas in the storage bulb was freed from oxygen by repeated freezing out with liquid air and thorough evacuation to a pressure of less than 10^{-4} mm. Three separate preparations were used, with no perceptible variations in their reactivity.

The furnace consisted of extra heavy iron pipe, well insulated. The temperature, which was always high enough to keep all reactants gaseous, was determined by means of a standard chromel-alumel thermocouple in the circuit of a sufficiently accurate Leeds and Northrup potentiometer; the couple was placed in various positions within the furnace and showed only slight variations in the temperature. The heating current was manually regulated and in the course of a run of several hours' duration, the temperature did not vary more than $\pm 0.5^\circ$. Two types of reaction vessels were employed, one of volume 80 cc., the other 320 cc.; the thermojunction was placed in the interior of the latter type. Numerous individual bulbs were used. At the termination of a run, the bulb, if to be reused, was filled with warm dichromate-sulfuric acid solution to destroy the liquid condensate which appeared upon cooling the vessel and was allowed to stand for several hours, after which it was thoroughly washed. Each cell was provided with two outlets, one of which consisted of tubing of large diameter through which thorough evacuation of the heated vessel by means of a mercury vapor diffusion pump occurred; this tube was then sealed off at the cell. The other outlet was of 2-mm. diameter capillary which communicated to the manometer system and the butadiene supply.

A quartz spiral manometer in conjunction with a mercury manometer and one of sulfuric acid served for the experiments over the pressure range from 100 to 760 mm.; for the lower pressure range from 100 to 1.5 mm. the sulfuric acid manometer and a McLeod gage in combination with an especially designed gage were used.

This latter instrument consists of a very thin disk of mica of approximately 6 cm. diameter supported by two sheet lead rings (5 cm. I. D.; 6 cm. O. D.; 1 mm. thick) from two brass plates (6 cm. diameter; 4 mm. thick), each perforated with a 1-cm. hole. The ring on the reaction system side is sealed to both brass and mica with shellac. The five parts are clamped firmly by external braces. One of the orifices in the plates communicates to the reaction system through capillary tubing joined to the brass by hard wax on the exterior of a ground joint in a brass collar. On the opposite face of the other plate is screwed a two-pronged bracket which has a sharply defined groove running across the prongs. In this depression rests the edge of a razor blade, 2 mm. \times 12 mm.; to the

¹³ A large quantity of quite pure butadiene tetrabromide was generously given by Dr. I. E. Muskat for this investigation, for which the author expresses his sincere appreciation.

¹⁴ Muskat and Northrup, *THIS JOURNAL*, **52**, 4043 (1930).

"knife edge" is cemented a mirror, 2×4 mm. Through the hole in the plate beneath the bracket projects a tungsten wire, 1 cm. long, sealed to the center of the mica with wax; this wire, against which the mirror rests, tilts it at an angle slightly from the vertical. A glass cylinder, 4 cm. high, is sealed to the brass disk by picein wax which is also used to render air-tight the brass-lead-mica junction. The outer ground face of the cylinder is covered with a glass plate joined to it with heavy stopcock grease. A by-pass from the reaction system to the direct-reading manometer side completes the device. The image of a single-filament lamp is thrown upon the mirror and the reflection observed on a scale, in this case a meter distant. Outside of a certain unsteadiness the entire apparatus proved to be quite satisfactory for the low pressure experiments and responded to a 0.03 mm. pressure difference at a total pressure of 2.50 mm. with a 2-mm. scale deflection. The sensitivity is dependent on the thinness of the mica and the position of the wire point against the mirror. After practice it is found relatively easy to make proper mica disks. Increase in the size of the diaphragm would enhance the sensitivity but likewise increases the likelihood of bursting or, at least, of permanent deformation; this latter point is the most serious one and necessitates care in the manipulation of the gas entry. It was found possible by means of careful regulation not to exceed a ≈ 10 -cm. deflection on the scale and yet to introduce 100 mm. of gas within the period of a minute; a gage under such treatment proved to be quite good.

Butadiene from the storage system was condensed in an auxiliary trap with carbon dioxide-acetone mixture and then allowed to vaporize; it was possible to judge the approximate amount of liquid needed for any given experiment. After thorough evacuation of the reaction vessel, the large tube was sealed and the system, with continued pumping, allowed to attain constant temperature. In the high pressure runs air was admitted to the mercury manometer to the desired value. The pumps were cut off and the stopcock separating the auxiliary trap from the reaction system was then quickly opened and vapor allowed to enter in sufficient quantity to cause coincidence of the quartz fibers; the stopcock was closed and frequent readings of the pressure and time were made. For the low pressure measurements, the only variation necessary was the simultaneous entry of both the butadiene and the air to opposite sides of the diaphragm at rates which permitted keeping the image on the scale approximately fixed.

Data and Results

A long series of preliminary runs revealed that the pressure fell off to approximately half-value, suggesting dimer formation. Thus the experimental data were treated by application of the differential form of the bimolecular reaction rate equation

$$\frac{d p_B}{dt} = k(p_B)^2$$

Table I gives the data of a typical experiment and the constants calculated therefrom. The initial pressure, p_0 , was obtained in all cases by graphical extrapolation.

The increase in the value of k with time is much more strikingly shown in Fig. 1, Runs 15, 16, 17, 18. It will be noted that the curve is quite horizontal until approximately 70% conversion of monomer, at which point it begins to rise rapidly. This behavior characterizes all of the runs. It is undoubtedly due to a secondary polymerization of molecules of dimer with one another or with molecules of the monomer. That polymerization

TABLE I

80-CC. VESSEL; 326°					
Time, min.	Pressure, mm.	$k \times 10^{+3}$ ($\text{mm.}^{-1} \text{min.}^{-1}$)	Time, min.	Pressure, mm.	$k \times 10^3$
0	(632.0)		49.50	498.1	2.27
0.92	629.2	(1.54)	55.08	490.2	2.23
3.25	618.5	2.42	60.87	482.8	2.20
6.12	606.6	2.36	68.05	474.6	2.16
8.02	599.4	2.30	77.57	464.8	2.18
10.08	591.6	2.42	90.05	453.3	2.25
12.18	584.2	2.38	103.58	442.6	2.27
14.30	576.1	2.73	119.00	432.8	2.15
17.30	567.3	2.24	135.72	422.8	2.39
20.78	556.9	2.46	176.67	405.3	2.22
24.55	546.8	2.38	216.50	394.4	1.95
29.18	535.4	2.43	259.50	381.0	3.03
33.00	527.8	2.14	295	373.1	2.99
36.38	521.2	2.24	373	357.1	4.26
42.50	509.3	2.45			

proceeds beyond the formation of a dimer is shown by one experiment (No. 20) of which the initial pressure was 244.5 mm. and wherein the pressure

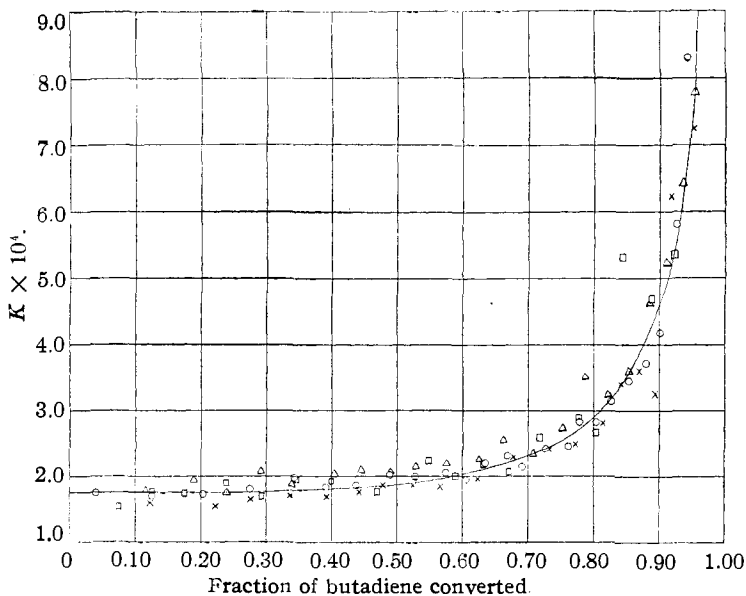


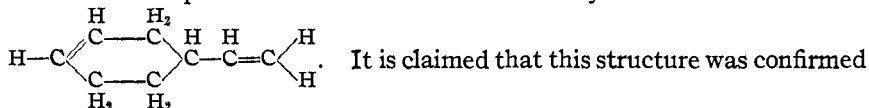
Fig. 1.—Rate constant *vs.* fraction of butadiene converted, 388°: ×, No. 15; △, No. 16; ○, No. 17; □, No. 18.

dropped to 40.0 mm. after a period of forty-five hours. It was observed that the colorless condensate obtained upon cooling to room temperature a reaction vessel containing a sample whose pressure had dropped below half

value, was more viscous than that obtained for shorter experiments; in a few very prolonged cases heavy oils were formed, and in one extreme instance the cell became coated with a brown iridescent film.¹⁵ The normal condensate, certainly consisting chiefly of dimer, was capable of reëvaporation to the original pressure. It is significant that this vapor phase reaction gives as a product a dimer which is quite stable, and that the primary association is so much more rapid than any of the subsequent processes. This is quite different from usual polymerizations wherein isolation of so relatively simple a product is generally difficult due to much more rapid secondary steps, indicative of the presence of extremely reactive molecules, which leads to long chain reactions. However, some liquid phase reactions (mentioned hereinafter) have definitely yielded dimers.

A study was made of the pressure increments corresponding to the deviations from the strictly bimolecular rate as computed for the early part of the reaction to see if these deviations might be kinetically interpreted, but due to the experimental errors in determining small pressure changes for relatively long time intervals, the effort yielded only semi-quantitative results.

Only one reference on the dimerization of 1,3-butadiene has been located. Hoffmann (with Tank)¹⁵ heated butadiene under pressure and obtained as a product a substance to which they ascribed the formula



by ozonization but unfortunately no experimental details or analyses are given.

Harries¹⁷ and Ostromuiskii¹⁸ reported that they obtained 2,6-dimethyl-1,5,7-octatriene upon carefully controlled polymerization of isoprene. Wagner-Jauregg¹⁹ claims on the basis of further experimental evidence that the material obtained by these two workers was identical with the *m*-menthadiene of Aschan.²⁰ It is interesting that also in the case of the polymerization of butadiene a dimer is obtained, and that the material may undergo further reaction.

In an effort to determine the precise composition of the dimer formed,

¹⁵ It may be recorded that one sample of pure liquid butadiene sealed in a tube and left undisturbed for one year, lost its extreme mobility and became very viscous; a white solid appeared in the liquid.

¹⁶ Hoffmann with Tank, *Z. angew. Chem.*, **25**, 1465 (1912).

¹⁷ Harries, *Ann.*, **383**, 206 (1911).

¹⁸ Ostromuiskii, *J. Russ. Phys.-Chem. Soc.*, **47**, 1928 (1915).

¹⁹ Wagner-Jauregg, *Ann.*, **488**, 176 (1931). See also Whitby and Crozier, *Canadian J. Research*, **6**, 203 (1932), for an extensive review and criticism of work on dimerization of isoprene.

²⁰ Aschan, *Ann.*, **439**, 221 (1924); *Ber.*, **57**, 1959 (1924).

the products of Runs 39, 40 and 41 (see Table III) were removed from the reaction system at periods corresponding to approximately 70% conversion of monomer to dimer; after this interval the secondary polymerization becomes much more prominent and the product is undoubtedly a mixture. The material obtained up to 70% conversion is probably quite pure. The gases in the reaction vessel were frozen out with liquid air in an auxiliary trap separated from the main system by a stopcock; the liquid was then carefully purified by repeated vaporizations, recondensations and removal of gases which could be pumped off when the sample was at room temperature. The light, colorless liquid obtained was then fractionally distilled *in vacuo* and the last third rejected; a slight light yellow gummy residue was present in each of the three cases. The amounts of the final product were very small, in some cases being only a small fraction of a cc.; nevertheless a very excellent set of determinations was made upon these samples by Miss Gertrude M. Ware under the supervision of Professor J. B. Conant (Table II).²¹

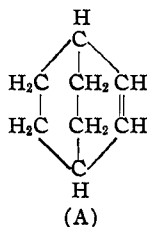
TABLE II

Run	d_{25}	(in Na light)	$\frac{n^2 - 1}{n^2 + 2} \frac{M}{d}$
39	0.867	1.469	34.75
40	.848	1.461	34.30
41	..	1.460	...

d_{25} is the density, n the refractive index and the last column gives the molecular refractivity, R , assuming the compound to be C_8H_{12} ($M = 108$). Calculated values of R for the various possible structures are as follows: for C_8H_{12} tricyclic, 32.55; dicyclic, one double bond, 34.28; open chain, two double bonds, 36.02; open chain, three double bonds, 37.74. While too great weight must not be given the data, due to the inherent errors, these figures indicate clearly that the compound in question is a dicyclic unsaturated hydrocarbon, for example (A). This structure may be derived from that proposed by Hoffmann.¹⁶ A distinction between the two (and, indeed, any other possible structure, such as may be arrived at by considering 1,4-addition at the conjugated double bonds) could only be made by a chemical analysis of the product, and it is proposed that this will be done in the near future. This unexpected conclusion is borne out by a consideration of the density figures in Table II.

The densities of cyclopentadiene, cyclohexane, cyclohexadiene, methylcyclohexene and dimethylcyclohexadiene (monocyclic C_8H_{12}) are all below 0.830. The addition of another cyclic system increases the density considerably, as campholene (monocyclic C_9H_{16}), 0.803, and nopinane (dicyclic C_9H_{16}), 0.861, show.

²¹ For the results given in Table II and aid in their interpretation, the author is deeply indebted to Professor Conant and Miss Ware.



Thus the data may be assumed to give, in the early part of the reaction, rate constants which represent the velocity of the association resulting in dimer formation. To obtain the average constant for a particular temperature, constructions of the type of Fig. 1 were made and an averaging curve plotted with extrapolation to 0% conversion. In Table III is presented a concise summary of data obtained in experiments with starting pressures in the range 100 to 720 mm.

TABLE III

Expt.	Temp., t, °C.	Initial pressure, mm.	$k \times 10^3$ (mm. ⁻¹ min. ⁻¹)		Comment
19	326	632.0	2.50	80-cc. vessel	
20	325	245.2			
21	326	105.9			
11	341	700.0	4.15	80-cc. vessel	
12	341	154.4			
13	343	356.3			
22	370	720.0	10.0	80-cc. vessel	
23	370	221.1			
39	370	389.1	11.3	320-cc. vessel	
40	370	375.1	11.1	320-cc. vessel	
41	370	407.2	10.7	320-cc. vessel	
15	388	378.0	17.5	80-cc. vessel	
16	388	378.0			
17	388	720.0			
18	388	206.0			
24	370.5	241.0	9.8	80-cc. packed cell	
25	370	211.2	10.9	80-cc.; 198.2 mm. propane added	
27	371	111.5	10.5	80-cc.; 590.6 mm. propane added	
26	371	192.7	10.1	80-cc.; 478.3 mm. nitrogen added	
28	373	198.0	13.0	80-cc.; 8.9 mm. oxygen added	
29	370.5	317.6	10.3	80-cc.; hexaphenylethane	

Figure 2 is a plot of $\log_{10} k$ against $1/T$ for the experiments listed above with the exception of the last six ($k = Ae^{-E/RT}$). The slope as drawn corresponds to an energy of activation of 24,700 calories; this value is presumably accurate to within 1000 calories. Application of the equation $k = AT^{-1/2}e^{-E/RT}$ (k in pressure units), which is the more exact relationship, gives for E a value $RT/2$ calories greater, namely, 25,300.

The homogeneity of the reaction was tested both in preliminary runs and, as indicated, by No. 24. In this case a cell filled with lengths of Pyrex tubing was used; the net volume was the same as in Nos. 22 and 23 (80 cc.) while the surface area was 675 sq. cm. as compared to 120, a 5.6-fold increase. No significant change in rate is revealed. This is an interesting variation from the results of Pease,⁸ who found a retardation of the ethylene polymerization by glass packing.

Added gases showed no effect. Tank propane at pressure ratios to that

of the butadiene of 1/1 and 5.5/1 caused no acceleration in rate. Similarly 99% pure nitrogen in a ratio 2.5/1 to butadiene was without evident result. These three experiments had exactly the same general trend as others at the temperature 371°; the rate constant gradually increased after a relatively long interval of constancy. Two runs were made wherein more butadiene was added during the course of the polymerization. No. 41 was one of these (see Table III) and the other, No. 6 (not given), showed the same trend. After 21.70 minutes, during which the rate constant increased from 10.7×10^{-5} (extrapolated value) to 12.3×10^{-5} for a pressure decrease corresponding to 49% conversion to dimer, 163.1 mm. of additional reactant was quickly added; the plot of k against time shows an unbroken

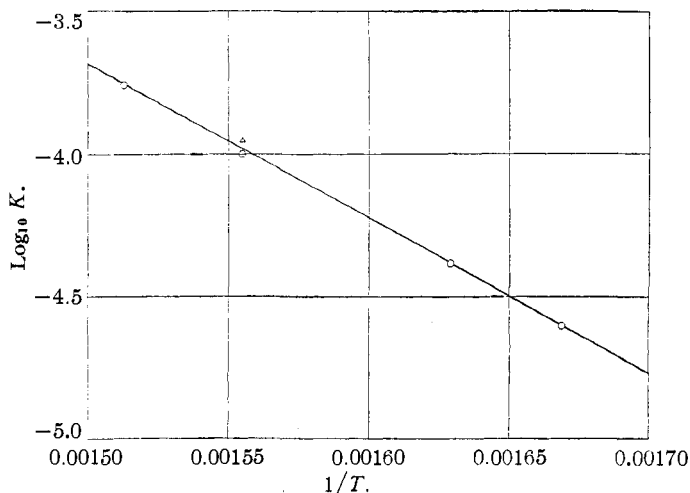


Fig. 2.—Log rate constant vs. $1/T$: Δ , 320-cc. vessel; \circ , 80-cc. vessel.

trend; the change of k is quite unvaried and progresses slowly, being 47.8×10^{-5} at 92.85 minutes for a calculated residual pressure of butadiene of 49.5 mm. This effect would indicate that in all probability the secondary polymerization is one involving the association of molecules of dimer with monomer. Likewise the group of runs with "added gas" shows that molecules of quite diverse character are incapable of changing the rate.

The work of Conant and Peterson²² shows conclusively that peroxides are extremely active catalysts in the promotion of the polymerization of isoprene at high pressures (3000–12,000 atm.). In order that the effect of oxygen might be determined, Run 28 (Table III) was made and it is seen that the rate is not radically altered by the presence of a considerable amount of oxygen. Traces of oxygen or of peroxides might have a very important effect and to examine this point, No. 29 was performed. Hexa-

²² Conant and Peterson, *THIS JOURNAL*, 54, 628 (1932).

phenylethane has a strong tendency to react with oxygen and was used with success by Conant and Peterson to lessen greatly the amount of peroxides in their isoprene, so that the rate was decreased ten-fold. Liquid butadiene was condensed on a sample of freshly prepared hexaphenylethane²³ and allowed to remain in contact with the solid for several minutes. The liquid was vaporized and its polymerization velocity determined. Even this treatment failed to alter the rate and it may reasonably be assumed that the general reaction is uncatalyzed.

The results of the low-pressure experiments are given in Table IV. Because of unsteadiness in the diaphragm gage it was necessary to increase progressively the temperature so as to obtain readable differences in pressure in sufficiently short time intervals. It was found that the precision of the measurements decreases greatly with decrease in pressures, as was indicated by the irregular plots of pressure *vs.* time. Runs 30 to 33 were quite consistent. For Runs 34 to 37, the averaging curve (pressure *vs.* time) was drawn in each case and the rate constant computed for several times in the interval over which the measurements were made. This procedure is not very satisfying and the values obtained are admittedly open to suspicion. Run 37 was of but 120 minutes' duration and only very approximate, and it was concluded that further extension of the pressure range was not feasible. Run 38 at the same temperature but with a "packed" cell of five times greater surface revealed that decomposition occurred under these conditions; blackening of the tubing slowly developed.

TABLE IV

Expt.	Temp., °C.	Initial pressure, mm.	Exptl. $k \times 10^{+6}$ (mm. ⁻¹ min. ⁻¹)	Extrap. $k \times 10^6$
30	380	105.5	15.0	
31	381	67.1	14.8	
32	381	29.22	15.5	14.0
33	381	32.78	15.2	
34	382	6.92	15	
35	394	2.98	20	20.4
36	414	2.53	60	35.8
37	436	1.50	290	62.2

In the last column is listed the value of k as determined by extrapolation of the curve of Fig. 2 which is expressible by the equation $\log k = -5390(1/T) + 4.394$. The experimental values of k for Nos. 36 and 37, coupled with the described behavior of No. 38, show definitely that the reaction is no longer simple beyond 394° and these data are not interpretable. It is to be observed that in the pressure range studied no falling off of the rate constant is noted.

²³ This material was received from Professor James B. Conant and Mr. B. F. Chow, and to them the author expresses his indebtedness.

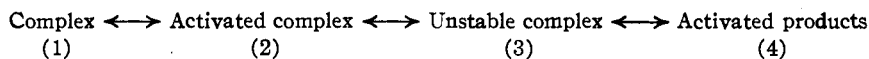
Discussion

The slope of the curve in Fig. 2 corresponds to an energy of activation of 24,700 cal. for the reaction $2C_4H_6 \rightarrow C_8H_{12}$. The Maxwellian distribution factor for molecules possessing in one degree of freedom this amount of energy at a temperature of 614°K. is 1.66×10^{-9} . The number of collisions per cc. in each second is given by the equation²⁴

$$Z = 2N^2\sigma^2 \sqrt{\frac{\pi kT}{m}}$$

wherein N is the number of molecules per cc., σ the diameter and m the mass of each particle. At $T = 614^\circ\text{K.}$ and a concentration of one mole per liter, a value of the diameter of 4.5×10^{-8} cm. gives $Z = 8.10 \times 10^{31}$. If each collision of suitably activated molecules results in reaction, the rate of disappearance of butadiene should be given by $2Z$ times the exponential since two molecules take part in each collision; this product is equal to 4.44×10^2 in liter moles⁻¹ sec.⁻¹. The value of k determined by experiment is 2.65×10^{-2} expressed in liter moles⁻¹ sec.⁻¹. The ratio of the observed and calculated rates is 1/16,800. If the value of 25,300 calories for E is used, the ratio becomes 1/10,300. These ratios, coupled with the data of Pease^{8,11} that the efficiency of the ethylene polymerization is 1/2000 and for the hydrogenation of ethylene, 1/10, strongly indicate the dependence of the efficiency upon the size and complexity of the molecule. As Kassel points out,⁹ although he conclusively shows the possibility with a high probability of the formation of association complexes by collisions of large molecules wherein energy and quantum conditions are satisfied, his treatment naturally neglects the determination of the total efficiency which will be dependent upon specific factors.

Thus the process may be considered as precisely the reverse of the unimolecular mechanism. The following series illustrates the idea



Unimolecular course: (1) \rightarrow (4)

- (1) \rightleftharpoons (2) Activation by collision and concurrent deactivation
- (2) \rightleftharpoons (3) Redistribution of energy
- (3) \rightarrow (4) Dissociation

Bimolecular course: (4) \rightarrow (1)

- (4) \rightleftharpoons (3) Association upon collision of suitably activated molecules; dependent upon orientation. Reversible
- (3) \rightleftharpoons (2) Redistribution of energy
- (2) \rightarrow (1) Stabilization upon collision.

The unimolecular course need not be discussed. The bimolecular or reverse reaction consists in the steps as listed. Two suitably energy-rich particles may, if properly oriented, combine with each other. This quasi-

²⁴ Tolman, "Statistical Mechanics," Chemical Catalog Co., N. Y., 1927, p. 242.

molecule may immediately decompose, or the excess energy may be redistributed among the various bonds, giving a more stable complex whose life would be sufficiently long to permit final stabilization by another collision. It may be further assumed that this stabilization will occur on every collision. It is essentially the assumption made in the unimolecular reaction theory and which has proved to be so useful. That no falling off of the rate (transition to a third order course) has been observed even at 3 mm. pressure, is perhaps not astonishing. The product formed here is of the same degree of complexity as azoisopropane, in the case of which no falling off of the rate has been detected even at 0.8 mm. pressure.²⁵

The fact that the hydrogen-ethylene reaction occurs on every tenth collision is excellent evidence in favor of Kassel's contention that for polyatomic molecules, quantization rules present no serious obstacles for association processes. Then, *a fortiori*, these limitations should be even less binding in the process of the production of yet more complex molecules such as butylene and the dimer here formed. Thus one is led to the conclusion that the lower yields observed in these cases are primarily due to a steric factor: the more complex are the associating molecules, the more precise must be their relative orientation at the moment of collision to achieve reaction.

It is planned to continue these polymerization studies to test further these ideas.

The Vapor Pressure of 1,3-Butadiene

After the completion of the polymerization experiments, there remained a considerable quantity of butadiene and inasmuch as the vapor pressure-temperature dependence had never been measured and there was immediately available the necessary apparatus, it was decided to determine the relationship.

The temperatures were measured by means of a triple junction copper-constantan thermopile in the circuit of the potentiometer used in the previous study. The instrument was calibrated by the use of the melting points of ammonia (-77.7°), mercury (-38.87°), carbon tetrachloride (-22.9°), carbon disulfide (-111.6°) and the ice point; the warm set of junctions of the thermopile was kept in ice water. All of these five points lay on a smooth curve. The butadiene was carefully redistilled three times before use and was then brought into a trap in immediate communication with a mercury manometer.

The data are given in Table V. Each point was checked, some as many as three times.

The plot of $\log_{10} p$ against $1/T$ is shown in Fig. 3; the equation of the line is $\log_{10} p = -1275 (1/T) + 7.615$. The heat of vaporization as determined therefrom is 5844 cal. The boiling point is found to be -4° .

²⁵ Ramsperger, *THIS JOURNAL*, **50**, 714 (1928).

TABLE V
VAPOR PRESSURE OF 1,3-BUTADIENE

Pressure, mm.	Temp., °C.	Pressure, mm.	Temp., °C.
9.2	-81.9	442.7	-17.0
11.0	-79.1	772.4	-3.1
156.9	-38.5	862.6	+0.5
327.5	-24.0		

Another experiment was performed to determine the melting point. Butadiene frozen with liquid air was allowed to warm slowly in a stirred chilled bath of gasoline, wherein the thermopile was immersed; the melting point of the solid was found to be -105° (average of two experiments).

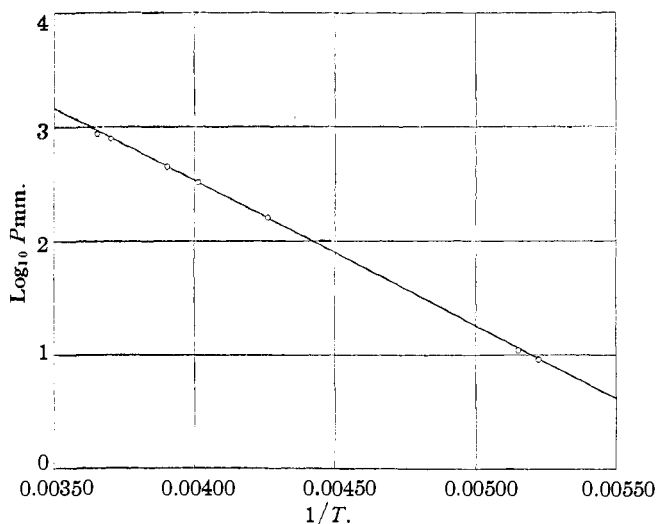


Fig. 3.—Vapor pressure of 1,3-butadiene.

The author is pleased to take this opportunity to extend to Professor G. B. Kistiakowsky his very sincere thanks for the active aid and stimulation received during the period of our recent association.

Summary

1. The kinetics of the thermal homogeneous polymerization of 1,3-butadiene have been investigated over the pressure range 720 to 1.5 mm. and a temperature interval of 326 to 436°. The reaction follows a strictly bimolecular course over the greater portion of the association.

2. The rate is expressible by the formula $\log_{10} k = -5680(1/T) + 7.673$ (k in liter·mole⁻¹ sec.⁻¹).

3. The kinetic mechanism is discussed.

4. The vapor pressure-temperature dependence of 1,3-butadiene has

been measured in the interval -82 to 0° ; the equation is $\log_{10} p = -1275(1/T) + 7.615$. (p in mm.); m. p. = -105° ; b. p. -4° .

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THE FIVE-ELECTRON PROBLEM IN QUANTUM MECHANICS AND ITS APPLICATION TO THE HYDROGEN-CHLORINE REACTION

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Calculations of Rollefson and Eyring¹ point to the probable formation of Cl_3 molecules when chlorine atoms collide with chlorine molecules. To determine from perturbation theory whether such triatomic molecules react more rapidly with hydrogen molecules than do chlorine atoms requires a knowledge of at least the five-electron problem, since five valence electrons change partners in the process. It has been suggested recently by Franck and Rabinowitz² and more explicitly by Bodenstein³ that the reaction $\text{H} + \text{Cl}_2 + \text{H}_2 = 2\text{HCl} + \text{H}$ might be an essential step in the photochemical combination of hydrogen and chlorine. To treat this reaction we again require a knowledge of the five-electron problem.

In the first part of the present paper we have used Slater's⁴ method to solve the problem of five electrons with spin degeneracy and have given the rules for finding the eigenfunction corresponding to an arbitrary number of valence bonds between designated atoms. The energy levels can of course be found for more than five or six electrons but the labor becomes extremely great. In the second part of this paper we examine the reactions which might be expected to play important roles in the hydrogen-chlorine reaction.

The Five-Electron Problem.—We shall assume that the reader is familiar with Slater's treatment of the three- and four-electron problems, and shall use the same notation. We refer those desiring a fuller treatment than that given here to the thesis by one of us (G. E. K.).

If the eigenfunctions of the five electrons are $a(1)$, $b(2)$, $c(3)$, $d(4)$, $e(5)$, then the product $a(1) b(2) c(3) d(4) e(5)$ is a solution of Schrödinger's equation when the atoms are far apart. Any one of the 120 eigenfunctions obtained by permuting the electrons will likewise be a solution. As the atoms approach one another certain linear combinations of these eigenfunctions will form the "zero order" approximation to the solution.

¹ Rollefson and Eyring, *THIS JOURNAL*, **54**, 170 (1932).

² Franck and Rabinowitz, *Z. Elektrochem.*, **36**, 794 (1930).

³ Bodenstein, *Trans. Faraday Soc.*, **27**, 413 (1931).

⁴ Slater, *Phys. Rev.*, **38**, 1109 (1931).